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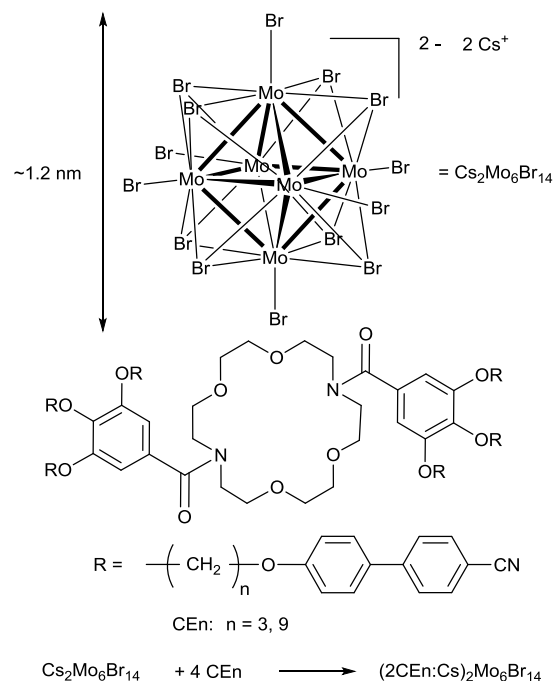
From Metallic Cluster-based Ceramics to Nematic Hybrid Liquid Crystals: A Double Supramolecular Approach

S. K. Nayak,^a M. Amela-Cortes,^a C. Roiland,^a S. Cordier,^a and Y. Molard^{a,*}

We describe a new supramolecular approach combining host-guest and electrostatic interactions to design hybrid materials containing polyanionic bulky inorganic compounds and showing liquid crystalline properties.

Hybrid organic-inorganic functional materials have become an intense field of research giving rise to a wide range of materials with applications in optic, electronic, biology, photovoltaic or medicine.¹ Controlling their structuration at the nanometric scale is a major challenge that implies the development of innovative bottom-up approaches. Thus, liquid crystalline (LC) hybrid materials are now in a stage of rapid development.² Indeed, they are easy to process, are able to spontaneously self-assemble over large areas into highly ordered domains and show structural defects self-healing abilities.³ Beside advantageous self-organizing properties, segregation phenomena that happen when inorganic and organic components are not interacting should be avoided to get homogeneous and stable materials with high inorganic content. Several strategies have been developed to minimize or suppress phase segregation while integrating bulky inorganic compounds into mesomorphic material, such as silver,⁴ gold⁵ or ZnO⁶ nanoparticles,⁷ polyoxometallates⁸ or transition metal clusters.⁹ The common approach is the covalent grafting of mesogenic promoters on the surface of inorganic entities. The second way concerns anionic inorganic compounds and consists in the replacement of inorganic counter-cations by functional organic ones bearing LC promoters.¹⁰ Basing our demonstration on the Cs₂Mo₆Br₁₄ nanometric cluster-based ternary molecular solid state compound, we propose in this work a new, softer and more straightforward strategy to integrate polyanionic inorganic bulky entities in LC materials. Discrete [M₆Qⁱ₈X^a₆]ⁿ⁻ (Q=chalcogen/halogen, X = halogen, M = Mo, Re or W) octahedral transition metal cluster compounds^{11, 12} are highly phosphorescent in the red-NIR area.¹³ In particular, A₂[Mo₆Br₈Br^a₆] salts (A = Cs, Rb or K), obtained by high temperature synthesis, can be further functionalized with organic ligands and/or integrated in hybrid materials.¹⁴ We use in this work several supramolecular interactions to build the hybrid polymolecular building blocks that will self-assemble: i) host-guest interactions between crown ether (CE) derivatives and alkali cations¹⁵ and ii) electrostatic interactions between the CE complex and [Mo₆Br₁₄]²⁻ to maintain the poly-ionic supramolecular assembly. Let us stress that combining luminescent lanthanides ions,¹⁶ transition metals or other ions

with mesomorphic or non mesomorphic CE to generate LC materials has already been reported in the literature. It usually leads to well-ordered structures in which new functionalities are provided by metallic cations complexed within the CE cavity.¹⁷ However, the integration of polyanionic or bulkier inorganic species in LC materials by our indirect method has never been reported so far. To obtain such material, we designed two functional diazacrown ether derivatives, namely CE₃ and CE₉ as depicted in **Scheme 1**. These organic compounds are made of six cyanobiphenyl (CB) units, a well-known liquid crystalline promoter, linked to the diazacrown via alkyloxy chains connected to a benzoic core. Using a short or long spacer between the mesogenic units and the complexing center modify the coupling between both motion moieties which should influence the self-assembling process.



Scheme 1. Schematic representation of diazacrown ether derivatives and complexes synthesized in this study.

CE_n were characterized by the usual techniques such as ¹H and ¹³C NMR, mass spectrometry and elemental analysis (see ESI for

experimental details). $\text{Cs}_2\text{Mo}_6\text{Br}_{14}$ salt was obtained by high temperature solid state synthesis using reported procedure with conform analytical data.¹¹ The synthesis of hybrids was achieved by mixing in solution the cluster salt with CE_n in a 1:4 ratio in order to fully complex Cs^+ cations. Indeed, it is well known that 2:1 sandwich or 3:2 club sandwich topologies are usually observed in this type of complexes.¹⁸ In our case, using lower cluster: CE_n ratio than 1:4 lead to non-homogeneous mixtures with phase segregation that was easily identified by polarized optical microscopy (POM) under UV irradiation (see ESI Fig S1 and S2). 400MHz ^1H NMR spectra recorded in solution for the complexes are nearly identical to their parent CE_n ^1H NMR spectra (see ESI Figure S3 and S4). This can be explained by the low binding affinity in solution of Cs^+ for diazacrown-[6]-ether derivatives¹⁹ which implies the introduction of a large excess of guest to observe noticeable variations in the ^1H NMR spectrum of the host.²⁰ Indeed, the size of our macrocycle cavity is more suitable for K^+ cation and only few works describe mesomorphic material containing 18C6 CE:Cs complexes.^{21, 22} Nonetheless, ^{79}Br and ^{133}Cs MAS solid state 600 MHz NMR experiments performed on $\text{Cs}_2\text{Mo}_6\text{Br}_{14}$ and both complexes either at 25°C or in the LC phase at 50°C for $(2\text{CE}_9:\text{Cs})_2\text{Mo}_6\text{Br}_{14}$ confirm the complexes formation (**Figure 1**).

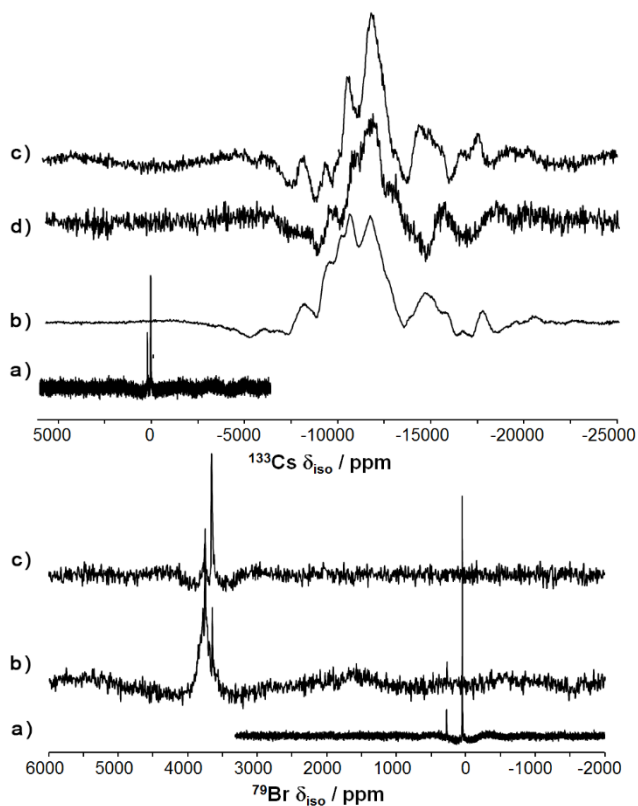


Figure 1. 150 MHz ^{133}Cs (top) and 78 MHz ^{79}Br (bottom) MAS NMR spectra of a) $\text{Cs}_2\text{Mo}_6\text{Br}_{14}$, b) $(2\text{CE}_3:\text{Cs})_2\text{Mo}_6\text{Br}_{14}$, c) and d) $(2\text{CE}_9:\text{Cs})_2\text{Mo}_6\text{Br}_{14}$ at 25°C and 50°C respectively.

While two sharp singlets located at 36.7 ppm and 216 ppm are observed in the ^{133}Cs spectrum of $\text{Cs}_2\text{Mo}_6\text{Br}_{14}$ (within the $\text{Cs}_2\text{Mo}_6\text{Br}_{14}$ crystal structure, Cs^+ location is shared between two

crystallographic positions and interacts with inner and apical Br ligands),¹¹ only one very broad (due to the non-crystallinity of the complex) and strongly shielded signal is observed in the complexes.

Although these signals are particularly large, their position and structuration are very similar for both complexes indicating that Cs^+ cations are surrounded by the same environment. Their strong shielding reflects an enhancement of the Cs^+ electronic density that is attributed to their interactions with the free electronic doublets of the macrocycle oxygen atoms. On the other hand, ^{79}Br NMR spectra are constituted by two singlets located at 51 ppm and 278 ppm for $\text{Cs}_2\text{Mo}_6\text{Br}_{14}$ that are broadened and drastically shifted to 3652 ppm and 3762 ppm for $(2\text{CE}_9:\text{Cs})_2\text{Mo}_6\text{Br}_{14}$ and 3654 ppm and 3757 ppm for $(2\text{CE}_3:\text{Cs})_2\text{Mo}_6\text{Br}_{14}$. These strong shifts indicate also that the electronic environment of the cluster anion is drastically modified and that there is no Cs-Br direct interactions within the complex.

Although, the binding affinity of Cs^+ for CE_n ligands might appear low, complexes remain very stable either under thermal treatment above their isotropization temperature (Fig S1 and S2) or after ageing for several months (no segregation observed in both cases). To give another proof that, the CE center is responsible of the homogeneity and stability of these materials and that they are not simple clusters-LC dispersion, we mixed $\text{Cs}_2\text{Mo}_6\text{Br}_{14}$ with the commercial 5OCB (4'-(Pentyloxy)-4-Biphenyl Carbonitrile) LC. As expected, we observed a full segregation of clusters within the nematic host (Fig S5).

The mesomorphic properties of CE_n and their respective complex with $\text{Cs}_2\text{Mo}_6\text{Br}_{14}$ were studied by differential scanning calorimetry (DSC), Polarized optical microscopy (POM) and temperature variable small angle x-ray scattering (SAXS). **Table 1** gathers the observed phase transition temperatures and thermodynamic data.

Table 1. Phase behaviour, transition temperatures and melting enthalpies of CE derivatives and their respective complexes taken from the 2nd heating.

Compound	Transition	T [°C]	ΔCp^b	ΔH^c	$\Delta\text{H}/\text{nb}_{\text{CB}}^c$
CE_9	g \rightarrow N	30.6	1.19	-	-
	N \rightarrow I	86.2	-	7.60	1.27
CE_3	g \rightarrow N	70.6	1.43	-	-
	N \rightarrow I	102 ^{a)}	-	-	-
$(2\text{CE}_9:\text{Cs})_2\text{Mo}_6\text{Br}_{14}$	g \rightarrow N	37.4	0.45	-	-
	N \rightarrow I	83.9	-	27.51	1.15
$(2\text{CE}_3:\text{Cs})_2\text{Mo}_6\text{Br}_{14}$	g \rightarrow N	76.1	1.14	-	-
	N \rightarrow I	113 ^{a)}	-	-	-

a) Temperature determined by microscopy; b) in KJ mol⁻¹K⁻¹; c) in KJ mol⁻¹; g: glass, N: nematic, I:isotropic.

All samples underwent three heating/cooling cycles to record DSC thermograms (see ESI Figure S6-S9). CE_3 and CE_9 show enantiotropic LC behaviour followed on cooling, by a glass transition. For CE_3 and its complex, the LC to I transition could not be detected by DSC. Therefore, the phase transition temperature reported is that observed by microscopy. It increases by 10°C for the complex compared to CE_3 which is commonly

ascribed to the complexation induced rigidification of the polymolecular system.²³ For CE₉ and its complex, the LC to I transition temperatures do not differ significantly. Although it might only be a coincidence, it could be imparted to the facts that i) the long alkoxy chains prevent strong interactions between the CE, the cations and the anionic clusters²⁴ and ii) Cs⁺ is too bulky to perfectly fit in the 18C6CE cavity. Indeed, it is also usually recognized that the stability of the induced mesophase depends strongly on the size of the cation.²¹ These points are corroborated by the calculated enthalpy values per mesogenic unit that are very similar and in the range of those observed for N to I transitions.²⁵

POM micrographs obtained in the LC phase for ligands and complexes are presented in **Figure 2**. While CE₉ and its complex show a typical nematic texture under white light, it was not possible to observe a very clear texture for (2CE₃:Cs)₂Mo₆Br₁₄ probably because of its high viscosity. In this last case, molecules were homeotropically aligned and a vanishing birefringence was observed only on shearing. SAXS experiments carried out between 90°C and 20°C are in good accordance with the nematic nature of all samples (see ESI Figures S10-S11 for temperature dependent diffractograms studies). It is well known that LC crown ether derivatives are usually well organized within the mesophase because of segregation phenomena between aromatic, polyether and aliphatic fragments leading to cubic, columnar or lamellar phases.²⁶ These phenomena should be more pronounced for CE₉ derivatives than for CE₃ because the long alkoxy chains allow a better decoupling between the motion of complexing centers and CB units. Generally, the introduction of alkali salts induces the formation of more ordered phases or can generate mesomorphism from non mesomorphic compounds.^{23, 27} Consequently, nematogenic CE, CE:alkali or CE:transition metal complexes are quite rare.^{23, 24, 28} In our case, the two complexes self-assemble in different ways as only (2CE₉:Cs)₂Mo₆Br₁₄ diffractograms present a small and relatively sharp scattering reflection at 4.1 Å that could correspond to the CE-CE distance in the sandwich complex and that may be indicative of a nematic columnar phase.²⁹

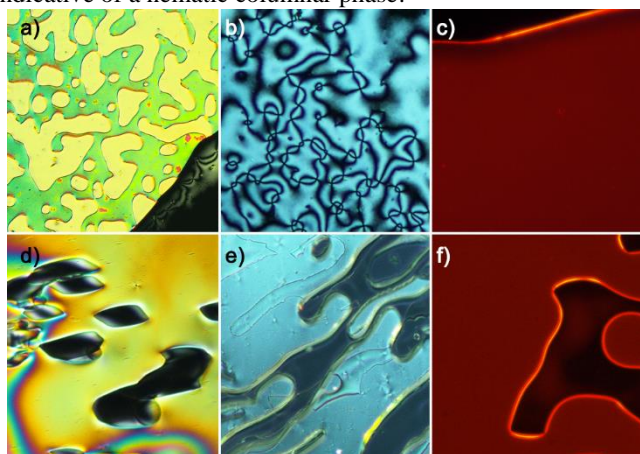


Figure 2. Polarized optical micrographs obtained for a) CE₉ (45°C), b) and c) (2CE₉:Cs)₂Mo₆Br₁₄ (80°C, b) white light, c) UV irradiation), d) CE₃ (80°C), e) and f) (2CE₃:Cs)₂Mo₆Br₁₄ (85°C, e) white light, f) UV irradiation).

UV Irradiation ($\lambda_{\text{exc}} = 380$ nm) of complexes in the LC phase leads to a homogeneous deep red emission characteristic of transition metal clusters that evidences the homogeneity of the material.

Absolute quantum yields were measured at 25°C using an integrating sphere on glassy samples and compared to the parent cluster in its powdered form. Calculated values (0.21 for (2CE₃:Cs)₂Mo₆Br₁₄, 0.15 for (2CE₉:Cs)₂Mo₆Br₁₄, 0.14 for Cs₂Mo₆Br₁₄ at $\lambda_{\text{exc}} = 380$ nm) are in the same range and show that the luminescence properties of the metallic cluster core are not altered either qualitatively or quantitatively by their introduction in the LC material (see ESI Figure S12-S14 for photoluminescence spectra).

Conclusions

In conclusion, we describe in this work, a new and straightforward approach to develop new hybrid materials merging the functionalities of nanometric inorganic anionic entities with the self-assembling abilities of organic liquid crystals. Our strategy combines host guest complex formation between Cs⁺ cations and diazacrown derivatives, with electrostatic interactions that maintain the functional inorganic anion within the material in close vicinity with the macrocycles. Homogeneous materials are obtained by simple mixing in solution of inorganic salts and organic ligands in the right proportions. By applying this innovative strategy to the ternary Cs₂Mo₆Br₁₄ solid state compound, we were able to generate a new hybrid material in which the bulky inorganic transition metal cluster keeps its luminescence properties, and remarkably, which possesses a nematic behaviour on broad temperature ranges. We must stress that these nanomaterials constitute the first example of poly-ionic nematic liquid crystal and we expect that our method can be generalized to other type of inorganic poly-anionic entities whose charge is counter-balanced by alkali or ammonium cations such as clusters with other nuclearity or polyoxometallates often obtained as alkali or ammonium salts.

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Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details, POM micrographs, NMR spectra, DSC thermograms, SAXS diffractograms, luminescence spectra, molecular model of 2CE₃:Cs. See DOI: 10.1039/c000000x/

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